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(54) USE OF SYNTHETIC CLAYS CONTAINING FLUORINE AND LITHIUM AS SOIL ANTI-REDEPOSITION AGENTS, IN DETERGENTS

(71) We, PFIZER INC., a Corporation organized under the laws of the State of Delaware, United States of America, of 235 East 42nd Street, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following state-

Modern day synthetic detergents are usually very effective in loosening soil particles in dirty clothing fabrics and removing the soil into the wash water during laundering operations, the soil being suspended in the aqueous detergent solution. However, some of this soil will be redeposited on the fabric during the laundering, causing a loss of whiteness in the fabric and a grey appearance.

One of the more common soil anti-redeposition agents used commercially today in detergent formulations is carboxymethylcellulose (referred to hereafter as CMC) or its alkali metal salt, which salt is usually the sodium 25 salt. Another common soil anti-redeposition agent used in commercial detergent formulations is polyvinylpyrrolidone referred to hereafter as PVP. However, both agent are relatively expensive, and in addition, do not seem to be uniformly effective against all types of fabrics; CMC not being uniformly effective on fabrics having synthetic fibers, and VIP not being totally effective on cotton fabrics.

The present invention provides a method of washing a fabric with a detergent formulation having soil anti-redeposition properties whereby the redeposition of soil upon a fabric from an aqueous washing solution of said formulation may be reduced, in which an improvement comprises employing a detergent formulation containing, as a soil anti-redeposition agent one or more compounds having the formula

 $[Si_8Mg_{0-x}Li_x(OH)_{1-y}F_yO_{20}]^{x(-)}.M_x(+)$

wherein x is from about 0.62 to 0.7, y is from about 0 to 1.22, and M is Na or Li. The invention also provides a detergent formulation, having soil anti-redeposition properties, containing as soil anti-redeposition agent one or more compounds having the formula stated above.

According to a further embodiment the invention also provides a detergent formulation which essentially consists of one or more alkali metal salts of fatty acids, one or more surfactants, one or more detergent builders and one or more compounds having the general formula stated above.

Most clay minerals, as found naturally, are in an impure state and the complete purification of some is difficult and expensive and, in some cases, impossible. Further, there are occasions on which the supply of a clay mineral of a particular chemical composition, either pure of impure, is insufficient. Thus, it is desirable to be able to manufacture synthetic claylike minerals in a substantially pure form and of pure white color.

It is of particular interest to be able to manufacture synthetic clay-like minerals having rheological properties similar to or better than those of hectorite, as natural hectorite has valuable properties but large quantities of hectorite are not available. In any event natural hectorite is mixed with impurities the removal of some at least of which is extremely difficult. The naturally-occurring clay, hectorite, has the formula (idealized)

[Si₈Mg_{5.3.1}Li_{0.66}(OH)₄O₂₀]Na_{0.66},

wherein F may replace some OH.

The compounds used as soil anti-redeposition agents in the present invention therefore have structural formulas very similar to, and including, that of natural hectorite.

Two methods are known for synthesizing hectorite-type clay minerals. One is described in Granquist and Pollack, "Clays and Clay Minerals", Natl. Acad. Sci., Natl. Res. Coun-

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1,376,379 65 cil Publ. 8, pp. 150-69 (1960). The other is vide the F ion separately. It has been surprisingly found that the compounds used as soil described by Strese and Hofmann in Z. Anorg. Chem., 247, pp. 65-95 (1941). anti-deposition agents in the present invention are more effective on fabrics made of syn-The compounds used as soil anti-redeposithetic fibres than the commercial agent CMC. tion agents in the present invention are advan-Fine particle sizes (e.g. 60 mesh and finer) are 70 tageously prepared by means of a process preferable in view of the normally short which comprises: laundering times (e.g. 10 minutes), to promote quick dispersibility of the soil anti-redeposi-(a) forming an aqueous slurry from tion agent in the detergent wash solution for i. a water-soluble magnesium salt, 75 maximum effectiveness. ii. sodium silicate, Of course, it is contemplated within the iii. sodium sodium carbonate OT scope of the present invention that the comhydroxide, pounds used as soil anti-redeposition agents iv. material delivering a soluble comaccording to the invention may be used in pound or compounds, containing admixture with commercial soil anti-redeposilithium and fluoride ions (e.g. LiF), or lithium ions only (e.g. LiCl, Li₂CO₃), and the aqueous slurry tion agents such as CMC and PVP to improve the properties of the commercial agents. The following wash test procedure employbeing formed by co-precipitation by ing a tergometer is used hereafter to evaluate slowly combining the magnesium salt and the sodium silicate and the the effectiveness of soil anti-redeposition agents in detergent formulations. The tergometer is a sodium carbonate or hydroxide, with heating and agitastandard instrument for measuring detergent efficiency. It usually comprises four numbered tion (e.g. 200°F.), the slurry containing at least the stoichiometric 1.5 litre pots containing agitators in which laundering conditions may be simulated. 90 amounts of all the cations and anions that are desired to be present in 1. Turn the tergometer heater switch on and adjust the thermostat to 120°F. Set agitator the final product; speed at 100 cycles per minute.

2. Weigh out one 1.50 gram of each deter-(b) taking the aqueous slurry so formed (e.g. after about 2-4 hours), washing it free from soluble salts, and filtering; gent formulation sample (which may contain (c) autoclaving the slurry (e.g. at a pressure a soil anti-redeposition agent) to be tested. 3. Add each weighed amount to a tergotoabout 100-250 psig and a corresponding steam temperature about 338—406°F.) for about 4—20 hours to meter bucket filled with 975 ml. of tap water. Agitate this mixture 30 seconds. 4. Add 25 ml. of a 2% solution, made by 100 crystallize the synthetic mineral-like mixing, into 1000 ml. of deionized water, 20 g. clay; and of a stock solution known by the Trade Mark (d) drying and grinding the finished pro-"Aquadag" which contains 22% solids of colloidal graphite in water, to each bucket con-Many variations of the above process can taining detergent and water. Agitate this for 105 be made by anyone skilled in the art. For example, step (a) can be performed in a pebble 30 seconds. 5-A. Add to each bucket the following mill without heating in which the slurry is formed by blending for about 1 hour and standard test fabric pieces identified with laundry ink. then processed according to steps (b), (c), and Eight white pieces of 80×80 cotton 110 (3"×6") folded in thirds.

Four white pieces of Dacron/cotton 7406 (d) above. Also, step (c) can be performed before step (b). Conveniently the following compounds can WRL (3"×6") folded in thirds.

Or—5—B. Add to each bucket the followbe employed in the processes according to the invention: Any suitable water-soluble maging 3"×6" fabric pieces folded in thirds. 115

nesium salt, for example, MgCl₂.6H₂O or Mg(NO₂)₂.6H₂O, or MgSO₄.7H₂O for Mg⁺⁺; Li₂CO₃ or LiF for Li⁺; HF acid or

LiF, H2SiF, or, for example, the sodium salt thereof, for F-, the latter also providing Na+ and silican ions; Na₂CO₃, NaÔH or sodium silicate for Na+, the latter will also provide silicon ions. Conveniently LiF is used as this will provide both Li⁺ and F⁻. Clearly, however, one can employ any lithium compound,

including LiOH, together with HF acid and achieve the same result in situ.

Other lithium salts, such as lithium chloride, can also be used to provide the Li+ ion and other fluoride compounds, such as NaF to pro-

Dacron/cotton 7406 W Dacron/cotton 7406 Cotton 400W Dacron spun 754 AW Nylon spun 358 Dacron/cotton 7402A Acetate Jersey S/113 Spun Viscose S/266 Orlon—75 S/862	RD	2 pieces 1 piece 3 pieces 1 piece	120
	Total	12 pieces	125

[&]quot;Dacron" and "Orlon" are Trade Marks.

6. Allow tergotometer to agitate 10 minutes. 7. After completion of cycles remove fabrics and agitators. Squeeze excess liquid from the fabric pieces.

8. Add 1000 ml. of 100°F, water to each bucket. Place the fabric pieces in same tergotometer bucket and rinse for 5 minutes at 100 cycles per minute agitation.

9. Remove the fabric pieces from the bucket and squeeze the excess water out and dry.

10. After the fabric is completely dry and conditioned to room temperature reflectance readings are taken using a standard Reflectometer. Using white tile as the reference standard, take the reading through a single thickness of 80×80 cotton. To take readings on Dacron/cotton arrange the four fabric pieces from a bucket in sandwich form for reflectance measurements. When comparing detergent formulations, lower reflectance readings after washing indicate lower SARD effectiveness, on a given test fabric.

The standard test fabrics used are identified by a number assigned by the supplier of these fabrics-Testfabrics, Inc., New York Cityand are as follows:

1. Dacron/Cotton-style 7406 WRL-65/35 shirting with Permanent press finish

2. Cotton—style W-Bleached 80×80 cotton print cloth.

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3. Dacron/Cotton—Style 7406---63/35 shirting.

4. Acetate Jersey-Style 113-All delustered filament.

5. Spun viscose—Style 266—Challis (print

cloth). 6. Dacron type 54-Style 754 AW-

100% spun fabric. Orlon—75—Style 862—Sand Weave.

8. Nylon spun 6.6—Style 358.

9. Dacron/cotton—Style 7402A—65/35

poplin (raincoat weight).

10. Dynel—Style 902—modified acrylic (this fabric sample was not used in all the tests).

Typically, the clay materials of the invention have relatively high surface areas compared to natural clays, being about 100-600 meters2/gram.

It has been known in the past that natural clays (for example that known by the Trade Name "Ben A Gel" and sodium bentonite BH-200) have soil suspending properties. In Example VIII, the soil anti-redeposition properties of these clays are compared with those of the compounds of this invention.

Effective amounts of soil anti-redeposition agents in commercial detergent formulations are typically 0.5—1.5%, based on the weight of the formulation. Preferably, about 1% by weight of the compounds of the invention are incorporated as SARD agent.

Use of the compounds of the invention in

detergent formulations contributes to the antistatic properties of the fabric.

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The following examples are provided for illustrative purposes and should not be interpreted as limiting the invention, the scope of which is defined by the appended claims.

Note that in the examples, surface area values (in square meters/gram or m²/g.) are based on low temperature nitrogen adsorption measurements. Also, crystallite size is expressed as a dimension in terms of angstrom units (A) of length, and is determined by X-ray Diffraction measurements. The crystallite is bounded by a change in electron density and the size is measured in a direction perpendicular to the characteristic 060 crystallographic plane of the (montomorillonite) unit

Examples I to IV illustrate the preparation of compounds which may be used as soil antiredeposition agents according to this invention. Example V illustrates detergent formulations and processes of washing not according to this invention for comparative purposes. Example VI illustrates detergent formulations and processes according to the invention. Example VII illustrates a detergent formulation and process according to the invention in Sample 1 and Test 1 and compares these with detergent formulations and processes not according to the invention. Example VIII is also comparative Samples and Tsests 2 and 3 being according to the invention.

EXAMPLE I. A compound having the formula

$$[Si_8Mg_{5.3}Li_{0.7}(OH)_4O_{20}].Na_{0.7}$$
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is prepared by first forming a slurry of the ingredients by coprecipitation as follows:

A stirred solution containing 5310 grams of MgSO₄.7H₂O dissolved in 25 liters of water and heated to about 205°F, in a 60 liter tank by means of steam coils, is precipitated over a 29 minute period with an alkaline solution having a temperature of about 140°F. and prepared by dissolving 6810 grams of N sodium silicate (8.6% Na₂O, 28.6% SiO₂) and 1285 grams of Na₂CO₃ in 25 liters of hot water. At the end of the precipitation period the precipitate slurry temperature is about 198°F. This is rapidly increased to and maintained at about 206°F, while the slurry is digested for 115 a period of 1½ hours during which time additional gas, taken to be CO2, is evolved from the slurry.

The slurry is then filtered and the resulting filter cake washed with 30 liters of water and allowed to drain on the filter. The washed filter cake, having a total weight of about 22,390 grams, is stirred to a viscous fluid into which is stirred 105 grams of Li2CO3 and a solution containing 150 grams of Na₂CO₃. 125

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Then this material is placed in pans and subjected to elevated temperature, about 365°F., at the corresponding gauge pressure, about 150 psi, in a steam operated, horizontal autoclave for about 16 hours. The autoclave product cake is cut into small pieces, dried, disintegated in a hammer mill to a fine powder (to about 5% plus 60 mesh). The product has a surface area of about 280 m²/g, and a crys-10 tallite size of 117Å.

EXAMPLE II.

A compound having the chemical formula

 $[Si_8Mg_{5.3}Li_{0.7}(OH)_4O_{20}] \cdot Li_{0.7}$

is prepared by following the procedure of Example I except that 210 grams of Li₂CO₃ is used in place of 150 grams of Na₂CO₃ and 105 grams of LiCO₃, and the autoclaving time is 21/4 hours. The product has a surface area of about 443 m²/g, and a crystallite size of 20 110Å.

EXAMPLE III. A compound having the formula

 $[Si_8Mg_{5,3}Li_{0,7}(OH)_{2,78}F_{1,22}O_{20}]$. Na_{0,7}

is prepared by following the procedure of Example I, except that 84 grams of LiF and 88 grams of NaF are used in place of 105 grams cf Li₂CO₃ and 150 grams of Na₂CO₃, and the autoclaved product is hammer mill ground to a fine powder (to about 5% plus 60 mesh). The final product has a surface area of 316 m²/g. and a crystallite size of 98Å.

EXAMPLE IV. A compound having the formula

 $Si_8Mg_{5.38}Li_{0.02}(OH)_3FO_{20}$]. $Na_{0.02}$

is prepared as follows (note that reference to gallons below are British Imperial gallons):

- (a) 60.68 pounds of magnesium sulphate heptahydrate are dissolved in 60 gallons of cold water and pumped into a reaction vessel having a nominal capacity of 200 gallons.
- (b) 11. 57 pounds of sodium silicofluoride and 5.44 pounds of lithium carbonate are added to the vessel and the mixture brought to a temperature of 95-98°C. with steam jacket heating and continuous
- (c) 44.17 pounds of anhydrous sodium carbonate are dissolved in 120 gallons of hor water (ca 60°C.) in a separate tank and 55.48 pounds of sodium silicate (Pyramid No. 1) are added; the mixture is then stirred.

(d) The solution containing the sodium carbonate and sodium silicate is fed into the reaction vessel via a separate entry port sited either on the lid or at the side close to the lid, of the reaction vessel, slowly over a period of 6/7 hours using a pump with a variable speed drive. (Rate of addition=17/20 gallons per hour). Continuous stirring and steam jacket heating are applied throughout the addition.

(e) The reaction time of 20 hours is commenced following the completion of the addition of the sodium carbonate/sodium silicate solution and after a reaction temperature of 95-100°C, has been reached.

(f) At the end of the reaction time, the charge is let out of the vessel into a suitable holding tank and allowed to settle overnight, following which the liquor is syphoned off.

(g) The settled reaction mixture is filtered on a plate and frame press at a cake formation pressure of 60 p.s.i.g., and washed with cold mains water at a pressure of 40 p.s.i.g., for a period of 20—22 hours.

(h) The washed filter press cake is dried in a Mitchell drier (steam heated) at a temperature of 105—110°C.

(i) The dried cake is ground in a Mini-Kek mill and the product passed over a 60 mesh vibrating screen. The fraction greater than 60 mesh is returned to the Mini-Kek mill for further grinding and this operation is repeated until less than 1% greater than 60 mesh remains on the screen.

The final product has a surface area of 367 m²/g. and a crystallite size of 110Å. Also a 2% dispersion of the final product in water has the following properties:

plastic viscosity (25°C.) 12.5 centipoises yield value 61 dynes/cm² 10-minute gel strength 186 dynes/cm²

The final product belongs to the class of 100 clay materials manufactured by Laporte Industries Ltd., England, called Laponite B. When mixed with 6% by weight of tetrasodium pyrophosphate it is called Laponite S, thus rendering the mixture sol-forming in water.

EXAMPLE V.

The standard wash procedure previously described is followed in Tests 1-4 in which the detergent samples 1-4 identified in Table 1 are tested.

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TABLE 1

Datamant	C 1.	- XY -
Detergent	Sambi	: INO.

	1	2	3	4
Colgate Detergent Base	1.485 g.	1.484 g.		1.484 g.
C.M.C.		0.015 g.		
Ajax Detergent			1.5 g.	
P.V.PK-30 (Average molecular weight 4	(0,000)			0.015 g.

Note in Table 1 that Ajax detergent has the following composition shown in Table 2.

	TABLE 2.		The Colgate Detergent base has the same	
	Anionic surfactant	10 wt. %	composition as Ajax, but with no soil anti-	
	Nonionic surfactant	2	redeposition agent.	15
5	Soap (e.g. sodium or potassium	•	In this and the following Examples CMC	
	stearate)	2	and PVP have the meanings hereinbefore	
	Sodium tripolyphosphate	3 <i>5</i>	assigned to them and polyvinyl alcohol is	
	Sodium Silicate	7	referred to as PVA.	
	Soil-antiredeposition agent (mix-		The following reflectance readings for each	20
10	ture of CMC and PVA) `	1	of the four samples identified in Table 1 are	
	Sodium sulfate	33—3 <i>5</i>	given for Tests using step 5A (Table 3) and	
	Water	810	for Tests using step 5B (Table 4).	

TABLE 3

	Average Reflectance	Reflectance after washing			
Fabrics	Before Washing	Test 1	Test 2	Test 3	Test 4
Dacron/cotton— 7406 WRL 1st Piece	89.13	66.07	69.14	73.06	78.09
Dacron/Cotton— 7406 WRL 2nd Piece	88.92	65.94	68.06	73.19	79.21
Dacron/Cotton— 7406 WRL 3rd Piece	89.16	65.58	68.19	72.53	78.62
Dacron/Cotton— 7406 WRL 4th Piece	89.02	67.47	69.27	73.64	77.75
Cotton—400W	94.08	41.37	61.34	66.28	52.80
Cotton—400W	94.39	43.60	60.01	64.02	52.14
Cotton—400 W	94.22	44.11	61.94	64.61	52.98
Cotton—400 W	94.18	45.26	61.63	65.35	52.11
Cotton—400 W	94.97	43.55	61.42	65.13	52.10
Cotton—400 W	95.03	43.39	61.87	65.10	52.99
Cotton —400 W	95.21	43.50	60.93	64.73	51.87
Cotton—400 W 8th Piece	94.20	43.36	60.80	65.75	52.11

TABLE 4

	Average Reflectance Before	Reflectance after Washing			
Fabrics	Washing	Test 1	Test 2	Test 3	Test 4
Dacron/Cotton— 7406 WRL 1st Piece	91.69	69.19	70.51	76.22	78.09
Dacron/Cotton— 7406 WRL 2nd Piece	91.18	70.52	72.03	78.10	79.21
Dacron/Cotton—7406	92.61	41.84	44.65	52.19	62.59
Cotton—400 W 1st Piece	94.19	46.52	64.72	66.97	53.36
Cotton—400 W 2nd Piece	94.30	47.08	65.45	64.49	53.53
Cotton—400 W 3rd Piece	93.71	45.98	63.90	67.22	52.27
Dacron Spun 754 AW	90.86	77.67	77.95	81.31	82.03
Nylon Spun 358	89.19	73.02	75.21	77.39	82.84
Dacron/Cotton 7402A	87.43	27.99	27.05	28.28	31.07
Acetate Jersey S/113	90.11	31.34	32.25	48.32	73.65
Spun Viscose S-266	91.75	68.21	73.84	78.56	77.56
Orlon-75-S/862	89.89	83.32	81.77	83.25	84.32

EXAMPLE VI.

The standard wash procedure is similarly followed as in Example V, except that step 5B fabrics only are tested and the detergent

formulation tested contains 1.485 g. of Colgate detergent base and 0.015 g. of the following soil anti-redeposition agents:

 Sample No.	Soil Anti-redeposition Agent
1	Mixture of the compound pre-prepared in Example IV +6 wt.% of TTSP*, the mixture ground to -325 mesh.
2	Compound prepared in Example III.

^{*} Note: TTSP means tetrasodium pyrophosphate. This is added to render the compounds prepared in Example IV as a sol in water.

Reflectance values before and after washing using Samples 1 and 2 respectively in Tests 1 and 2 are presented in Table 5 below.

TABLE 5

Reflectance Before Washing	Test 1	Test 2
Dac/Cotton 7406 WRL 1st Piece	91.54	91.32
Dac/Cotton 7406 WRL 2nd Piece	91.62	91.20
Dac/Cotton 7406 WRL Cotton 400 W Cotton 400 W Cotton 400 W Dacron 754 W Nylon 358 Dac/Cotton 7402 A Acetate Jersey S113 Spun Viscose S266 Orlon-75-S862	91.22 93.17 93.48 93.63 91.44 90.09 88.49 89.96 88.61 87.90	91.89 93.71 93.08 93.16 91.19 90.02 88.80 89.93 88.70 87.06
Reflectance After Washing		
Dac/Cotton 7406 WRL 1st Piece	72.75	72.98
Dac/Cotton 7406 WRL 2nd Piece	72.69	74.86
Dac/Cotton 7406 Cotton-400W Cotton-400W Cotton-400W Dacron 754 W Nylon 358 Dac/Cotton 7402A Acetate Jersey S113 Spun Viscose-S266 Orlon-75-S-862	64.04 52.69 49.74 51.81 82.70 73.59 45.29 76.87 81.13 84.17	68.36 56.12 56.82 54.40 81.64 75.40 51.44 68.54 78.85 84.87

EXAMPLE VII.

This example compares the effectiveness in detergent formulations of various soil antiredeposition agents among which are natural

clay materials such as Ben A Gel and Sodium Bentonite BH—200 typical analyses of which are as follows:

	Ben A Gel	Sodium Bentonite, BH-200
SiO_2 Al_2O_3	56.5 0.2	64.73 20.82
Fe ₂ O ₃ TiÖ ₂	0.2	3.44 0.14
MgO CaO	25.8 2.8	2.38 0.49
Na ₂ O, K ₂ O Li ₂ O	2.6 1.1	2.92
Cl F	2.5 1.0	
Ignition Loss	$\frac{7.7}{100.4}$	99.75
Crystallite Size Å	200	238
Surface Area, m ² /g.	52	31

The standard wash procedure is similarly followed as in Example V, except that step 5B fabrics only are tested and the detergent formulations tested contain 1.38875 g. of Colgate detergent base and 0.01125 g. (0.75%) of a soil anti-redeposition agent identified as follows:

Sample 1: Compound of Example 1
Sample 2: Ben A Gel
Sample 3: Sodium Bentonite BH—200
Sample 4: CMC

Reflectance values before and after washing in Tests 1 to 4, using Samples 1 to 4 respectively are presented in Table 6 below

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TABLE 6
Reflectance Before Washing

Kenetance before washing					
	Test 1 Test 2 Test 3 Test				
Dac/Cotton 7406 WRL-1	91.20	90.70	91.65	91.46	
Dac/Cotton 7406 WRL-2	90.85	90.91	91.85	91.62	
Dac/Cotton 7406	91.89	91.07	92.28	91.68	
Cotton 400W-1	93.87	93.90	95.54	93.74	
Cotton 400W-2	93.43	93.58	94.88	93.73	
Dacron Spun 754 AW	89.75	89.27	89.53	88.73	
Nylon Spun 358	91.55	90.73	90.28	90.82	
Dac/Cotton 7402A	87.77	91.96	91.99	86.03	
Acetate S/113	94.05	93.09	93.89	91.53	
Viscose S/266	91.64	92.26	92.18	92.18	
Orlon-75-S/862	87.56	88.15	87.19	87.19	
Dynel S/902	87.55 Reflectance	85.93 After Washing	86.60	86.48	
Dac/Cotton 7406 WRL-2	78.95	78.80	76.62	77.67	
Dac/Cotton 7406 WRL-2	80.31	76.29	76.75	76.13	
Dac/Cotton 7406	57.21	49.84	56.58	49.46	
Cotton 400W-1	47.35	45.39	48.32	58.72	
Cotton 400W-2	45.64	42.39	47.42	59.45	
Dacron Spun 754 AW	79.13	64.87	71.71	66.08	
Nylon Spun 358	75.96	74.28	73.35	75.26	
Dac/Cotton 7402A	34.17	26.05	27.96	26.10	
Acetate S/113	29.57	22.24	26.43	20.41	
Viscose S/266	79.48	67.50	73.13	77.88	
Orlon-75-S/862	83.48	79.94	81.08	81.47	
Dynel S/902	80.43	77.55	79.05	76.21	
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EXAMPLE VIII.

The standard wash procedure is similarly followed as in Example V, except that some of the step 5B fabrics only are tested and the

detergent formulation tested contains 1.485 g. of Colgate detergent base and 0.015 g. of the following compounds as soil anti-redeposition agents:

Sample No.	Soil Anti-Redeposition Agent
1	CMC
2	Compound prepared in Example II
. 3	Mixture of the compound prepared in Example V $+6$ wt.% of tetra-sodium pyrophosphate (TTSP), the mixture ground to -60 mesh,

Reflectance values before and after washing obtained in Tests 1 to 3 using samples 1 to 3 respectively are presented in Table 7 below.

TABLE 7

Fabrics	Average Reflectance Before Washing	Reflectance After Washing		
		Test 1	Test 2	Test 3
Dac/Cotton 7402A	88.4	26.2	38.4	34.6
Nylon Spun 354A	93.3	70.4	64.4	72.6
Dacron Spun 754AW	89.5	61.4	74.6	70.5
Cotton 80×80 400W	95.2	48.7	42.5	37.8
Dac/Cotton 7406	94.2	48.0	55.6	49.1
Dac/Cotton 7406WRL	93.0	58.3	58.2	61.4

WHAT WE CLAIM IS:—

1. In a method of washing a fabric with a detergent formulation having soil anti-redeposition properties whereby the redeposition of soil upon the fabric from an aqueous washing solution of said formulation may be reduced, the improvement which comprises employing a detergent formulation containing, as a soil anti-redeposition agent, one or more compounds having the formula

$$[\,Si_{_{8}}Mg_{_{6-x}}Li_{_{x}}\!(OH)_{_{4-y}}F_{_{y}}O_{_{20}}]\,\,\,x(-)\,.\,M_{x}(+)$$

wherein x is from about 0.62 to 0.7, y is

from about 0 to 1.22, and M is Na or Li.

2. The improvement according to claim 1, wherein said detergent formulation consists essentially of one or more alkali metal salts of fatty acids, one or more surfactants, and one or more detergent builders.

3. The method of claim 2, wherein x is 0.62,

y is 1 and M is Na.

4. A detergent formulation having soil antiredeposition properties containing, as a soil anti-deposition agent, one or more compounds having the formula

$$[Si_sMg_{6-x}Li_x(OH)_{4-y}F_yO_{20}]$$
 x(-). $M_x(+)$ 35

wherein x is from about 0.62 to 0.7, y is

from about 0 to 1.22, and M is Na or Li.
5. A detergent formulation consisting essentially of one or more alkali metal salts of fatty acids, one or more surfactants, one or more detergent builders, and as soil antiredeposition agent one or more compounds of the formula

$$[Si_8Mg_{6-x}Li_x(OH)_{4-y}F_yO_{20}]$$
 x(-). $M_x(+)$

wherein x is from about 0.62 to 0.7, y is from about 0 to 1.22, and M is Na or Li. 6. A method as claimed in claim 1 and sub-

stantially as described herein with reference to any one of Examples VI (Tests 1 or 2), VII (Test 1) and VIII (Tests 2 or 3).

7. A detergent formulation as claimed in claim 4 and substantially as described herein with reference to any one of Examples VI (Sample 1 or 2), VII (Sample 1) and VIII (Sample 2 or 3).

8. A detergent formulation as claimed in claim 4 wherein the soil anti-redeposition agent is the compound produced according to any one of Examples 1—4.
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20